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SINGLE STAGE NITRIFICATION-DENITRIFICATION

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SINGLE STAGE NITRIFICATION-DENITRIFICATION

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The removal of 75-84% of the nitrogen from primary wastewaters was achieved in a single stage activated sludge process. The two-pass reactor was operated with a food to mass ratio (F/M) of approximately 0.1 gm BOD_5/day/gm MLVSS. The air was applied on a 30-minute cycle first to one reactor pass then to the other pass. Mechanical mixers suspended the mixed liquor solids when the air was not applied. The D.O. concentration varied from 0.0 mg/l without air to 2-3 mg/l during aeration. In June with a 9-hour detention time in the reactor, the residual pollutant concentrations averaged 23 mg/l of COD (90% removal), 3.8 mg/l of total nitrogen (84% removal) and 7.8 mg/l of suspended solids (93% removal). In February, with a 12-hour reactor detention time, the residual pollutants averaged 25 mg/l of COD (89% removal), 6.0 mg/l of Total N (75% removal) and 14 mg/l of suspended solids (87% removal). Since the nitrate from nitrification was used to remove BOD_5 from the wastewater, the process advantages for single stage nitrification-denitrification included the reduction in the amount of air needed to achieve BOD_5 removal and nitrification; the minimizing of supplemental organic carbon sources for denitrification; and the elimination of clarifiers in staged nitrification-denitrification.

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SINGLE STAGE NITRIFICATION-DENITRIFICATION

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

This work describes an alternate method for removing organic (BOD), nitrogen (NH_3), and phosphorus (P) pollutants from the aqueous environment. This wastewater treatment approach achieves significant removals of organics and nitrogen pollutants from wastewater with minimum use of energy and scare chemicals such as methanol.

A. W. Breidenbach, Ph.D.
Director
National Environmental
Research Center, Cincinnati

ABSTRACT

The removal of 75 to 84 percent of nitrogen from primary wastewaters has recently been achieved in a single stage activated process at the EPA-DC pilot plant in Washington, D.C., without the use of supplemental organic carbon. The removal was achieved in a two pass biological reactor in which the D.O. concentration was varied from 0 to 2 to 3 mg/l. The air was applied on a 30-min cycle, first to one reactor pass then to the other pass. Mechanical mixers suspended the mixed liquor solids when the air was not applied to the pass. At F/M of approximately 0.1 gm BOD_5/day/gm MLVSS, a mixed culture of carbonaceous (BOD_5 removal), nitrifying, and denitrifying organisms developed. With the D.O. at 2 or above, the nitrification readily occurred. When the D.O. decreased to near zero, denitrification occurred. The process also produced efficient organics removal with more than 85 percent of the COD removed from primary wastewater.

The COD/TKN ratio in the wastewater entering the reactor controlled the amount of nitrogen removal. With a COD/TKN ratio of 10, 84 percent removal of total nitrogen from the primary effluent was achieved in the summer and 75 percent removal in the winter. When the COD/TKN ratio was reduced to about 7.5 by $FeCl_3$ treatment in the up-stream primary process, the nitrogen removal across the biological process in the summer decreased to 67 percent. The data suggest that increases in the COD/TKN ratio would further increase nitrogen removal.

Laboratory kinetic studies on the mixed liquor solids revealed that the denitrification kinetic rate controlled the reactor design. The nitrification rate constants varied from about 0.03 gm of NH_3-N removed/gm of MLVSS/day at 15.5°C to 0.11 gm of NH_3-N removed/gm of MLVSS/day at 27°C. The denitrification rate constants during the initial anaerobic cycle varied from about 0.03 gm NO_3-N removed/gm MLVSS/day at 15.5°C to 0.055 gm NO_3-N removed/gm MLVSS/day at 25°C. The denitrification rate constant then declined to lower levels after the organic carbon was consumed by the biological reaction. In the winter with District of Columbia wastewater, bulking growth occurred in the reactor and required low overflow rates of 12.2 m/d (300 gpd/ft^2) to capture the solids in the clarifier. Bulking conditions did not occur during summer operations. The mixed liquor solids in the summer exhibited initial settling velocities of 3.7 to 4.3 m/hr (12 to 14 ft/hr).

This report was submitted in partial fulfillment of Contract No. 68-01-0162 by the Department of Environmental Services, Government of the District of Columbia, under the sponshorship of the Environmental Protection Agency. Work was completed as of September 1973.

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SECTION I

CONCLUSIONS

The removal of 75 to 84 percent of nitrogen from primary wastewaters has recently been achieved in a single stage activated sludge process (30,000 to 50,000 gpd) at the EPA-DC pilot plant in Washington, D.C., without the use of supplemental organic carbon. The removal was achieved in a two pass biological reactor in which the dissolved oxygen concentration was varied from 0 to 2 to 3 mg/l. The air from the blower was applied on a 30-min cycle, first to one reactor pass then to the other pass. Mechanical mixers suspended the mixed liquor solids when the air was not applied to the pass. At an F/M ratio of 0.1 gm BOD_5/day/gm MLVSS, a mixed culture of carbonaceous (BOD_5 removal), nitrifying and denitrifying organisms developed and essentially complete nitrification was achieved. With the dissolved oxygen at 2 or above, the nitrification readily occurred. When the dissolved oxygen decreased to near zero, denitrification occurred.

The COD/TKN ratio in the wastewater entering the reactor controlled the amount of nitrogen removal. With a COD/TKN ratio of 10:1, 84 percent of the total nitrogen, based on the primary effluent, was removed in the summer and 75 percent in the winter. When the COD/TKN ratio was reduced to about 7.5 by $FeCl_3$ treatment in the up-stream primary process, the nitrogen removal across the biological process in the summer decreased to 67 percent. The increased removal of particulate organics with the $FeCl_3$ treatment in primary sedimentation reduced the relative amount of the organic carbon source available for denitrification and left more NO_3^--N in the process effluent. The data suggest that increases in the COD/TKN ratio would further increase nitrogen removal.

Laboratory kinetic studies on the mixed liquor solids revealed that the denitrification kinetic rate controlled the reactor design. Nitrification rate constants at a given temperature generally remained the same during repetitive aerobic-anaerobic cycles. The denitrification rates, however, decreased as the residual carbon was consumed by the biological reactions.

In the winter with District of Columbia wastewater, bulking growth occurred in the reactor and required low overflow rates of 12.2 m/d (300 gpd/ft^2) to capture the solids in the clarifier. Bulking conditions disappeared during summer operations. The mixed liquor solids in the summer exhibited initial settling velocities of 3.7 to 4.4 m/hr (12 to 14 ft/hr).

Since the nitrate from nitrification was used to remove BOD_5 from the wastewater, the process advantages for this single stage two basin nitrification-denitrification process included:

- the reduction in the volume of air needed to achieve nitrification and BOD_5 removal

- The minimizing and, with further study, potential elimination of supplemental organic carbon sources required for complete denitrification

- substantial nitrogen removal without special recycle of the mixed liquor

- the elimination of intermediate clarifiers required in staged nitrification-denitrification

Even if bulking limits winter operations, application of the dissolved oxygen cycle to existing extended aeration plants in warm weather reduce requirements to achieve nitrification and BOD_5 removal. The reduced air requirement potentially lowers conventional operating costs.

SECTION II

RECOMMENDATIONS

The process applied to the District of Columbia wastewater produced bulking sludge conditions in the winter operations. Other continuously aerated activated sludge processes at the District of Columbia have also exhibited bulking sludge conditions for various operating approaches, especially in the winter. Work is needed to determine, in general, why bulking sludge conditions occur and, specifically, whether the anaerobic-aerobic operation of the single stage nitrification-denitrification approach contribute to the bulking. Additional work is also needed on the kinetics of the nitrification, denitrification, and carbonaceous utilization to develop an optimum anaerobic-aerobic process configuration.

SECTION III

INTRODUCTION

Nitrification by autotropic bacteria (Nitrosoma and Nitrobacter) achieves a maximum rate[1] in the activated sludge process at dissolved oxygen concentrations of approximately 2 mg/l or above. The rate decreases to zero as the dissolved oxygen concentration decreases to zero. In contrast, while denitrification by facultative bacteria occurs in both anoxic and aerobic systems, the most rapid denitrification occurs with dissolved oxygen concentrations of zero and with ample sources of readily available organic carbon to serve as electron donors for the bacterial reduction of the nitrate or nitrite.

In biological treatment of wastewaters, oxidation of carbonaceous material, nitrification, and denitrification all occur within a single process if sufficient bacterial solids retention time is provided for development of the nitrifying organisms. Unfortunately, optimum process operating conditions for oxidation and for subsequent denitrification are thermodynamically antagonistic. That is, the presence of the more powerful oxidant oxygen (electron acceptor) suppresses the use of NO_3^- (electron acceptor) in the biological oxidation of the carbonaceous material in the wastewater. In conventionally aerated biological systems, efficient oxidation of the carbonaceous and nitrogenous materials, in either a single or two stage process is achieved under aerobic reactor conditions. The aerobic conditions produce the nitrate product but also remove the organic materials that act as readily available electron donors for rapid denitrification. In addition, the dissolved oxygen in the water significantly suppresses or minimizes the biological reduction of the nitrate or nitrite as they are produced.

Clearly, while in municipal wastewaters, the biological potential exists for both nitrification and denitrification without supplemental organic carbon sources, the operating conditions usually employed in aerobic biological processes produce efficient carbonaceous removal and nitrification but not efficient denitrification. Thus, the purpose of this work was to select and to demonstrate the operating conditions for the activated sludge process at the EPA-DC Pilot Plant in Washington D.C., that would produce efficient nitrification and denitrification with the indigenous carbonaceous material in the wastewater acting as the electron donor during denitrification.

SECTION IV

TREATMENT APPROACHES FOR NITROGEN REMOVAL

As early as 1962, Ludzack and Ettinger[2] recognized the possibility of using the organic carbon in wastewater as the electron donors for the bacterial reduction of the nitrate or nitrite products of biological oxidation. They used alternate anaerobic and aerobic zones within a single activated sludge reactor to provide for a period of low or zero dissolved oxygen for denitrification. In the process, effluent reactor mixed liquor with the nitrate product from the aerobic (or second) zone was recycled to the reactor influent zone, which was operated under anaerobic conditions. With ample supply of influent carbonaceous material, the nitrate acting as an electron acceptor was reduced to nitrogen gas during the biological oxidation of the carbonaceous material. The amount of denitrification was controlled by the rate of recycle of the mixed liquor from the aerobic zone to the anaerobic zone. In the study, the maximum nitrogen removal exceeded 60 percent.

In an alternate approach to achieve nitrification-denitrification, Wuhrman,[3] in a two zone reactor, located the anaerobic zone after the aerobic zone. In this approach which did not require recycle of mixed liquor, the endogenous activity of the activated sludge mass provided the organic carbon (electron acceptors) for the denitrification. Wuhrman reported nitrogen removals of more than 90 percent in his approach. According to Barnard,[4] others studies, however, could not repeat Wuhrman's removal. Apparently the endogenous activity of the activated sludge mass provided low amounts of available carbonaceous material for the denitrification and produced a low endogenous denitrification rate.

Since these early approaches, various biological systems for maximum nitrogen removal have been evaluated. Barth et al.,[5] developed a reliable three stage approach that consisted of three independent activated sludge reactor-clarifiers for sequential carbonaceous removal, nitrification, and finally denitrification. Since essentially all of the carbonaceous material was removed from the wastewater after nitrification, a supplemental organic carbon source, such as methanol, was required to produce denitrification in the final stage. A short aerobic zone or basin was employed between the denitrification reactor and the final clarifier. The aerobic zone prevented clarifier sludge bulking, which is caused by the N_2 flotation of the sludge from the denitrification reactor, and aerobically removed small amounts of excess methanol from the water. Barth's three stage approach applied at the Environmental Protection Agency-District of Columbia (EPA-DC) pilot plant in Washington, D.C., provided very efficient all-seasons operations,[6] with average total nitrogen residuals in the filtered (dual media) final effluent of 1.5 mg/l as nitrogen.

Balakrishman and Eckenfelder[7] proposed a contact stabilization modification of the three stage system to eliminate the need for methanol in denitrification. In their approach, the nitrified effluent from the second stage and the solids from the first stage (contact-aeration) clarifier were mixed in a basin for stabilization and denitrification before final clarification. The NO_3^- in the nitrified effluent acted as an electron acceptor in the biological stabilization (oxidation) of the active contact-aeration sludge and, thus, was reduced to nitrogen gas without a supplemental organic carbon source. Nitrogen removals of approximately 80 percent have been reported for this approach.

In 1972, Matsché[8] reported significant removals of nitrogen in an "oxidation ditch" activated sludge plant at Vienna-Blumental. The plant employed two basins in series with rotors for aeration and mixed liquor recirculation. Examination of the detailed data[9] on the plant clearly revealed the required high solids retention time and operating conditions for efficient nitrification-denitification. The dissolved oxygen concentration at the rotors were above 2 mg/l and essentially zero before the next rotor. The wastewater recirculation, inherent in rotor operation, provided a supply of carbonaceous material for the denitrification. The alternating high-low dissolved oxygen tension, the appropriate solids retention time, and the presence through recirculation of readily available organic carbon, provided the conditions for efficient nitrogen removal.

Recently, three studies, including the work reported here, have been independently completed in developing a conventional single reactor-clarifier system for removing nitrogen without supplemental organic carbon. Barnard[4,10] developed a single reactor-clarifier system using four basins alternating from anaerobic to aerobic conditions in series with a single final clarifier. In the system, the first two basins employed the Ludzack-Ettinger approach. Mixed liquor from the second basin (nitrifying aerobic conditions) was recycled at rates up to four times the influent plant flow to the first basin (anaerobic conditions) for partial denitrification. The third basin (anaerobic conditions) employed Wuhrman's endogenous denitrification. The final basin (aerobic conditions) prevented final clarifier sludge bulking, potentially caused by the N_2 production in the third basin. Barnard's single stage (multi-basin) reactor clarifier approach provided more than 90 percent removal of nitrogen without the use of methanol.

Christensen[11] proposed a two basin, single, reactor-clarifier process with appropriate solids retention for nitrification- denitrification without a supplemental carbon source and without mixed liquor recirculation. The process employed alternating aeration in first one basin and then the other to produce the alternate high-low oxygen concentration needed for efficient nitrification-denitrification. To provide readily available organic carbon, the influent wastewater and the settled activated sludge, recycled from the clarifier, was alternately added to either of the two basins during the basin's anaerobic portion of the plant's aeration cycle. In the system, the process flow always proceeded from the anaerobic (nonaerated) to the aerobic basin to the clarifier, but the physical direction of the flow through any basin reversed itself with the change from anaerobic to aerobic operating conditions. Reportedly,[11] the approach consistently produces effluents with total nitrogen content of 2 to 5 mg/l.

SECTION V

EXPERIMENTAL PLAN AND PROCEDURES

This approach to achieve nitrification-denitrification in a single, activated sludge reactor-clarifier with the wastewater organic carbon used for denitrification consisted, simply, of providing alternate periods of aerobic and anaerobic conditions within the reactor and operating the reactor at sufficiently low food-to-microorganism ratios (high solids retention times) to ensure a nitrifying population within the mixed liquor culture. To provide the alternating aerobic-anaerobic conditions while continuously operating the air compressor, an activated sludge reactor (Figure 1) in the EPA-DC pilot plant was divided into two equal basins operating in series. Each basin, with a water depth of approximately 3.35 m (11 ft), provided a detention time of 3.55 hr at a process flow of 189 m^3/d (50,000 gpd). Air was supplied alternately to each basin; first to one basin and then to the other on a 30-min cycle. The dissolved oxygen in the basins was manually controlled at between 2 and 3 mg/l during aeration and rapidly decreased to zero during the anaerobic period.

In each basin, two mechanical mixers, operated at 30 rpm, suspended the mixed liquor solids without any significant surface aeration of the wastewater. Air was supplied through a 0.95 cm (3/8-in.) orifice below a 30.5 cm-diameter (12-in.) by 1.53 m long (5 ft) Kenics* static mixer.

For additional experimental options, an effluent mixed liquor recycle pump and two other small basins with water depth of 3.35 m (11 ft) were also provided. The effluent mixed-liquor recycle pump was used to increase the amount of NO_3^- in the first basin of the reactor, through recycle of the second basin mixed liquor. It was only used during the first month of operation. The first optional basin with a 0.89-hr detention at 189 m^3/d (50,000 gpd) and with a 30-rpm mixer was covered for anaerobic operation and equipped with a methanol feeding system for denitrification of any residual nitrate. The second optional basin with a Kenics static mixer and a 0.89-hr detention at 189 m^3/d (50,000 gpd) provided continuous aeration to remove excess methanol and to prevent N_2-induced sludge bulking in the clarifier. The optional basins were used only in the last month of the experimental work.

For most of the work, the mixed liquor was settled in a center feed clarifier, which was a convented thickener with a conventional thickening mechanism. The clarifier, with a water depth of 3.35 m (11 ft), provided an overflow rate of 21 m/d (520 gpd/ft^2) at a 189 m^3/d (50,000 gpd) process flow. To permit relevelling of the clarifier, for about one month of the experimental work. An alternate center feed clarifier without a thickening mechanism was used with an overflow rate of 27 m/d (665 gpd/ft^2) at a 189 m^3/d (50,000 gpd) flow.

The pilot plant start-up began in December 1972. The study continued through September 1973. For most of the study, primary effluent from the District of

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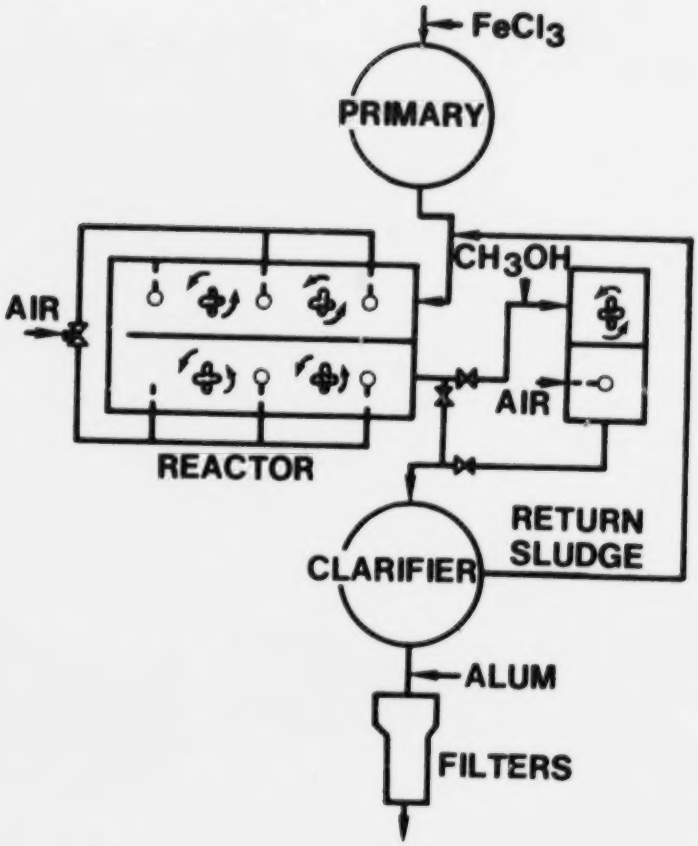


Figure 1. Pilot plant system for single stage nitrification-denitrification

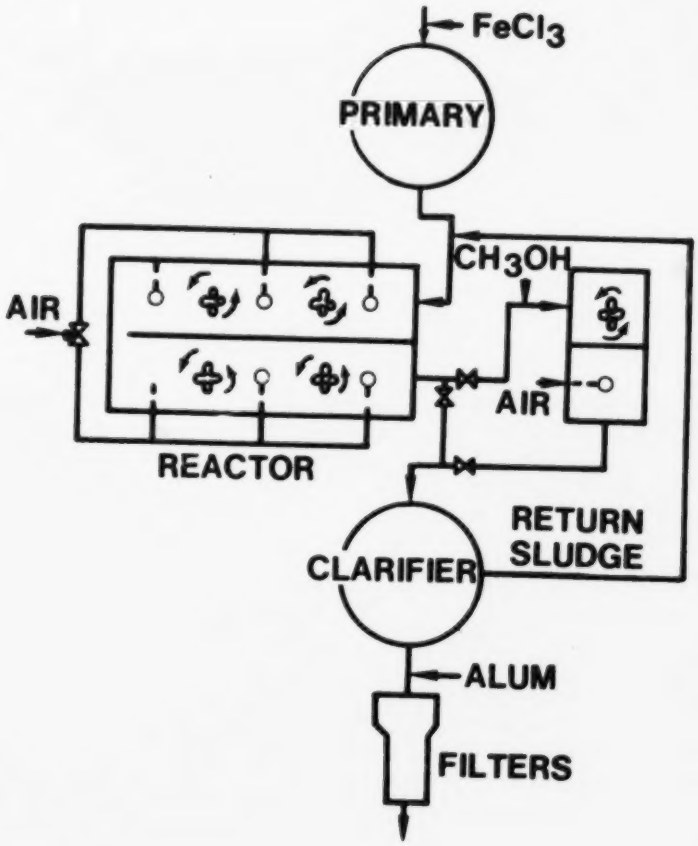


Figure 1. Pilot plant system for single stage nitrification-denitrification

Columbia Water Pollution Control Plant was fed at various steady flows to the activated sludge reactor. During July through September, however, pilot plant primary effluent was fed on a diurnal cycle with a 2:1 maximum-to-minimum flow to the biological reactor. In July and August, 45 mg/l of $FeCl_3$ was added for phosphorus removal to the influent raw wastewater. Also in July and August, the secondary effluent was filtered through dual media filters at an average loading (2:1 diurnal flow cycle) of 7.8 m/hr (3.2 gpm/ft^2). Alum at a 20 mg/l dose was added to the secondary effluent in a mixing chamber immediately ahead of the filters. The filter media consisted of 61 cm (24 in.) of 1.2- to 1.4-mm coal over 30.5 cm (12 in.) of 0.6- to 0.7-mm sand.

In evaluating the process, appropriate samples were manually composited over a 24-hr period on Tuesday, Wednesday, and Thursday. Samples collected on Friday-Saturday and Sunday-Monday, except those for BOD_5 analysis, were composited over a 48-hr period. BOD_5 samples were always composited over a 24-hr period. All samples were stored at 3^{o}C to minimize biological activity. All samples, except those for BOD_5 and suspended solids analyses, were preserved with one drop of H_2SO_4 per 30 ml of sample while they were held in storage.

The BOD_5 was determined by the dissolved oxygen probe method;[12] the ammonia[12] and the nitrate-nitrite,[13] by the Technicon autoanalyzer; and the total phosphorus, by the persulfate method.[14] All other analyses employed "Standard Methods."[15]

Batch settling tests on the mixed liquor were periodically conducted in a stirred (10 rph) settling column, 15.3 cm (6 in.) in diameter and 2.3 m (8 ft) long. Batch kinetic studies were performed in the laboratory to determine kinetic rates for nitrification and denitrification. The studies were performed by mixing 1 to 2 liters of the recycle solids with the primary effluent in a ratio similar to that existing in the process. A water bath was used to ensure that the temperature of the kinetic test remained the same as that in the process. The mixture was aerated, usually for 30 min, and then mixed with a magnetic stirrer under anaerobic conditions, usually for 30 min, for several cycles. The changes in NH_3-N NO_3^--N were monitored by Technicon analyses to determine the kinetic rates of the alternating nitrification and denitrification.

SECTION VI

PROCESS PEFORMANCE

In mid-December 1972, the operation of the system was started with District of Columbia primary effluent as feed and with a seed of partially nitrifying activated-sludge. The start-up system consisted of two basins in series and the final clarifier with a standard sludge recycle system. On January 1, 1973 with complete nitrification established, the controlled dissolved oxygen cycling was applied across the two reactor basins. The steady influent flow was increased from 110 m^3/d (29,000 gpd) to 163 m^3/d (43,000 gpd) on January 3. The internal recycle of the mixed liquor was started on January 5, at a recycle flow equal to 50 percent of the influent flow. The process behaved as expected. With the cycling of the dissolved oxygen concentration, the denitrification rapidly increased and the nitrate residual (Figure 2) decreased to about 4 mg/l as nitrogen. With the initiation of the recycle of the mixed liquor from the second basin to the first, the residual nitrate concentration continued to decrease to less than 2 mg/l as nitrogen, but the NH_3-N gradually increased to about 2 mg/l. The denitrification did not cause any immediate sludge bulking in the process. Unfortunately, the process, operating at a low F/M ratio, began to develop a poorly settling sludge that, by January 19, forced a reduction in process flow to 110 m^3/d (29,000 gpd) to prevent excessive solids carryover. Microscopic examination of the sludge indicated the probable presence of both Sphaerotilus and Nocardia organisms. (Both organisms have been identified at various times in other activated sludge processes at the EPA-DC pilot plant.)

On January 19, the internal recycle of the mixed liquor also was discontinued. With the elimination of internal mixed liquor recycle and with the lower flow, the effluent NH_3-N decreased to less than 0.5 mg/l and the effluent NO_3-N increased to about 4.5 mg/l. The poorly settling sludge, however, continued as a major operating problem throughout the winter months and persisted into spring. In spite of the process settling characteristics, the first month's operation clearly demonstrated process nitrogen removal potential without a supplemental organic carbon source and without mixed liquor recycle.

The average monthly operating conditions are summarized for the 9 months of the study in Table 1. The average operating conditions for January represent only the low flow operation used for about one half of the month. In addition, from mid-March through April 6, an alternate clarifier without a thickening mechanism was employed with about a 28 percent increase in the overflow rate. The average clarifier overflow rates given for March and April, however, are those of the original clarifier.

During the 9 months, the reactor was operated with a F/M ratio of approximately 0.1 gm BOD_5/day/gm mixed liquor volatile suspended solids (MLVSS). In the winter, long detention periods (12 hr) and somewhat lower F/M ratios provided time for the slower biological reactions and permitted low overflow rates needed for solids separation of the bulking mixed liquor in the clarifier. In April and May, attempts were made to eliminate the bulking growth. From about mid-April to May 20, the process was operated with continuous aeration (thus,

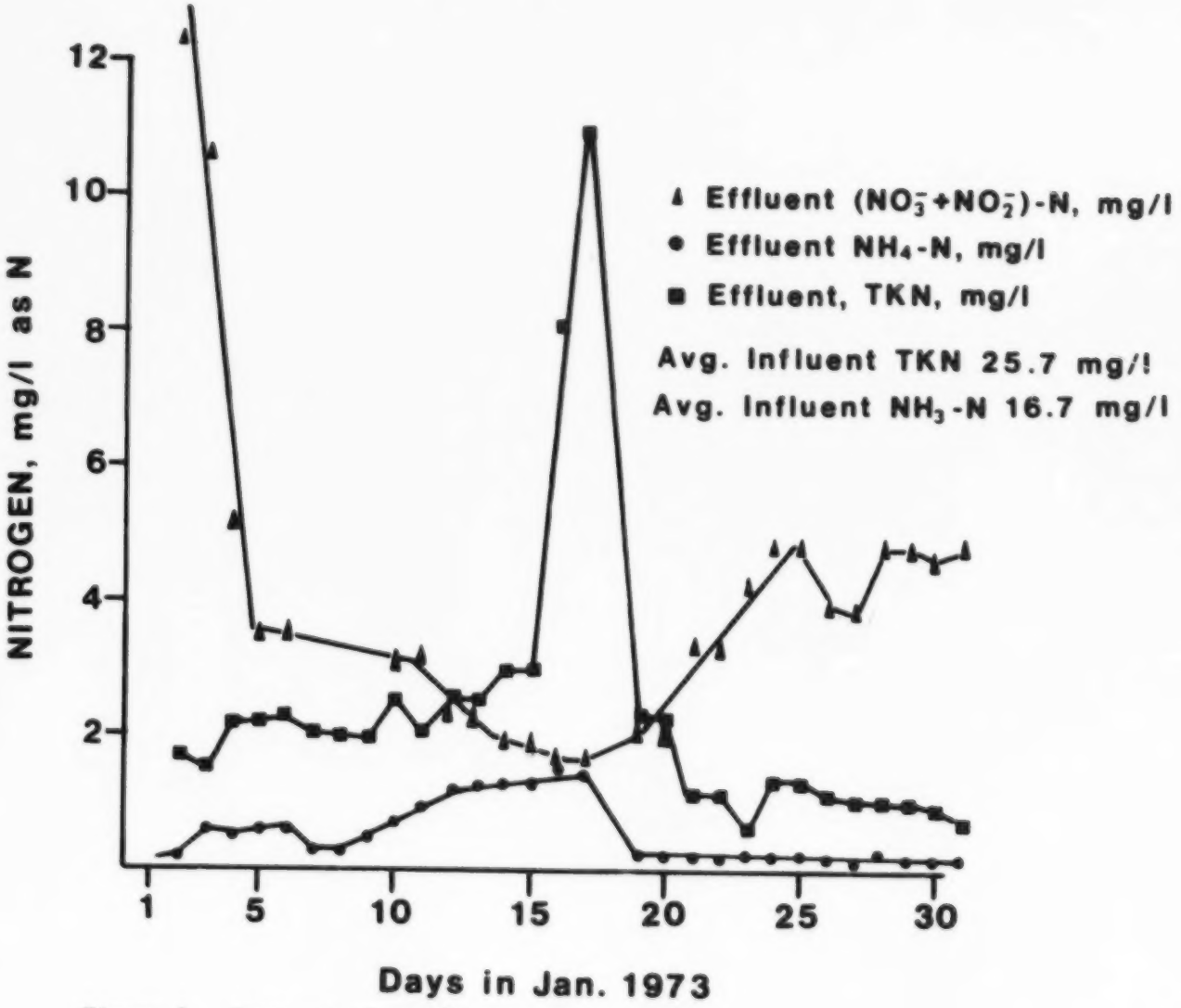


Figure 2. Start-up of aerobic-anaerobic cycle

Table 1. OPERATING CONDITIONS

	Detention Time, hr	SRT, days	F/M, $\frac{\text{gm BOD}}{(\text{gm MLVSS})(\text{Day})}$	MLSS, mg/l (% vol.)	Overflow Rate, m/d
Jan.	12.3	-[a]	.072	3510(74)	12.3
Feb.	12.3	33	.066	3980(73)	12.6
March	12.3	24	.10	2950(73)	12.3
April	12.4	-[a]	.081	3540(67)	12.3
May	10.5	21	.089	4270(67)	14.1
June	8.8	18	.105	4010(69)	17.4
July	6.8	15	.093	3040(64)	22.2[b]
August	6.6	-[a]	.089	3200(57)	23.1[b]
Sept.[c]	8.7	-[a]	0.11	3700(65)	23.1[b]

[a]Solids retention time (SRT) not given because of solids accumulations or unknown solids losses.

[b]Average overflow; 2:1 maximum-to minimum flow variation.

[c]Two optional basins (one for methanol denitrification, the other for re-aeration) were placed on stream.

without anaerobic periods) to "burn out" the bulking growth. The attempt was not totally successful but, with increasing water temperatures and summer operating conditions, by June the solids settling characteristics had improved. Summer operation was not plaqued with bulking growth. In the July and August operation, the $FeCl_3$ added to the primary process reduced the COD and total Kjeldahl nitrogen (TKN) as well as the phosphorus entering the biological process. The process flow and reactor solids were altered to maintain the desired operating F/M.

The organic, solids and phosphorus removals during the study are summarized in Tables 2 and 3. Clearly the process provided excellent organic and solids removal. Winter operation with bulking growth (January-April) did not prevent efficient organic and solids removal but did require low clarifier overflow rates. Since the process effluent contained nitrifying organisms, both the standard BOD_5 and the BOD_5 with nitrification inhibition by 0.5 mg/l of thiourea are included in Table 2. The COD removals ranging from 83 to 91 percent across the biological reactor were both consistent and excellent, even in September when methanol was added for residual nitrate removal.

The suspended solids removals (Table 3) ranged from 85 to 93 percent removal across the biological reactor-clarifier. With the $FeCl_3$ added in the primary in July and August, the removals across primary and secondary treatment averaged 95 percent. The phosphorus removals without specific chemical treatment varied from 25 to 47 percent across the biological reactor. These phosphorus removals were unusually high for biological treatment especially for operation at low F/M. Approximately 45 mg/l of $FeCl_3$, added into the primary process in July and August, produced approximately 85 percent removal of the phosphorus across primary and secondary treatment.

Nitrogen removals (Tables 4) revealed that the alternating nitrification-denitrification process in the winter ($15^{o}C$) produced about 75 percent nitrogen removal across the biological system without methanol. In June at higher twmperatures ($25^{o}C$), the removal increased to 84 percent of the nitrogen entering the biological reactor. The lower removals in April and May represent operation for a portion of each month (early April and late May) with aerobic and anaerobic conditions and for a portion of each month with continuous aerobic conditions. The lower nitrogen removals across the biological process in July and August (67 percent) occurred with altered operating conditions (Table 4). The operation for January through June was performed at steady flow and at COD/TKN ratios of approximately 10:1. With the addition of $FeCl_3$ in the primary process and with diurnal flow variation, the nitrogen removals across the biological process decreased significantly. In the most significant change, the $FeCl_3$ addition decreased the COD/TKN ratio from 10:1 to between 7:1 and 8:1. Although not shown in Table 5, the COD/NH_3-N ratio decreased even more sharply from approximately 18:1 to about 9:1. At present, more work is required over a range of F/M and COD/TKN ratios, preferably with automatic dissolved oxygen control, to determine more clearly the effect of the controlling variables [F/M ratio, COD/TKN or COD/NH_3-N ratios, and dissolved oxygen cycle (time and dissolved oxygen values)] on the process design and operation.

Filtration of the secondary effluent in July and August with 20 mg/l of alum

Table II. ORGANIC REMOVAL

	BOD			COD		
	Primary Influent, mg/l	Secondary Effluent, mg/l	Sec. (Inh) Effluent,[a] mg/l	Primary Influent, mg/l	Secondary Effluent, mg/l	% Removal
Jan.	96.5	20.4	-	246	40	84
Feb.	99	14.0	-	234	25.1	89
March	110	16.3	6.5	262	30.6	88
April	98.8	10.0	5.3	230	27.7	88
May	115	8.4	3.3	234	24.3	90
June	107	7.1	3.2	238	23.4	91
July[b]	51	7.7	3.8	119	20.9	83
August[b]	44.2	6.2	2.6	112	17.3	85
Sept.[c]	99	15.4	7.2	225	31.6	86

[a] BOD_5 test with 0.5 mg/l of thiourea for inhibition of nitrification.

[b] $FeCl_3$ in primary process reduced influent organic load.

[c] Methanol addition (18.6 mg/l) during September 5-12, with two optional reactor basins.

Table III. SOLIDS AND PHOSPHORUS REMOVAL

	Suspended Solids			P		
	Primary Influent, mg/l	Secondary Effluent, mg/l	% Removal	Primary Influent, mg/l	Secondary Effluent, mg/l	% Removal
Jan.	110	15.4	85	7.25	4.83	33
Feb.	108	14.3	87	7.12	4.33	39
March	128	15	88	7.10	3.76	47
April	120	13	89	6.22	3.69	41
May	109	11.8	89	7.24	5.03	27
June	112	7.8	93	7.14	5.32	26
July[a]	153	9	94	5.88	1.14	81
August[a]	197	10	95	5.78	0.88	85
Sept.	110	16	85	6.77	3.80	45

[a]With $FeCl_3$ in the primary process, the removals of solids and phosphorus is based upon the raw wastewater rather than on the primary effluent.

Table IV. NITROGEN REMOVAL

1973	Primary TKN, mg/l	Secondary Effluent				
		TKN, mg/l	NH_4 + -N, mg/l	(NO_3- + NO_2-)-N, mg/l	Total N	
					mg/l	% Removal
Jan.	25.7	2.28	0.53	3.99	6.27	76
Feb.	23.2	1.52	0.31	4.41	5.94	75
March	24.8	4.20	2.40	2.30	6.5	74
April	21.7	5.20	3.90	6.03	11.2	49[b]
May	23.3	1.36	0.31	8.25	9.61	59[b]
June	24.0	1.51	0.45	2.30	3.81	84
July[a]	15.0	2.14	1.63	2.72	4.86	67 (74)[c]
August[a]	14.9	1.23	0.59	3.74	4.97	67 (74)[c]
Sept.	22.6	10.2	9.4	0.22	10.4	54[d]

[a]The $FeCl_3$ in the primary process reduced the TKN in the influent to the biological reactor.

[b]Portions of each month operated with continuous aeration.

[c]% Removal based upon the raw wastewater.

[d]Methanol addition inhibited nitrification.

Table V. NITROGEN REMOVAL AND THE F/M AND COD/TKN RATIOS

Period	Temp., °C	F/M, gm BOD/gm MLVSS/day	COD/TKN	% Removal Total N
Jan.	14.0	0.072	9.6	76
Feb.	14.2	0.066	9.9	75
March	15.5	0.100	10.5	74
June	23.0	0.105	10.3	84
July	25.0	0.093	7.9	67
August	25.5	0.089	7.5	67
Sept.	26[a]	0.11	10	54

[a]Methanol addition inhibited nitrification.

[$Al_2(SO_4)_3 \cdot 14\ H_2O$] added ahead of the filters (Table 6) was chiefly effective for phosphorus removal. Average phosphorus residuals decreased by more than 50 percent with filtered residuals of 0.4 to 0.5 mg/l as phosphorus. The accumulated removals increased from approximately 85 to 93 percent. Filtration only modestly decreased other pollutant concentrations. The filtration removals of these pollutants from the secondary effluent ranged from 17 to 35 percent.

The settling characteristics and sludge production in the biological process is summarized in Table 7. The low production in April reflected solids accumulation to replace unknown solids losses in the transfer of operation from one clarifier to another in March and April. A high solids production in July represents excess solids wasting to maintain the desired F/M ratio for the decreased food input to the reactor during $FeCl_3$ addition in primary treatment. Solids production for August is not given because of an unknown solids loss (mechanical failure). The changes in the solids concentration of the recycled sludge revealed the presence or absence of the thickening device within the clarifier. The sludge volume index (SVI) (Table 7) and the initial settling velocities of the mixed liquor (Figure 3) clearly indicated the poor winter solids settling characteristics and the gradual disappearance of the bulking sludge in the summer. Because the bulking sludge problem occurred at low F/M operating conditions in several continuously aerated activated sludge studies in the EPA-DC pilot plant, the winter settling problems may not be related to the on-off aeration sequence for nitrification-denitrification.

Laboratory denitrification tests (Figure 4) revealed that methanol addition to the mixed liquor leaving the second reactor basin removed the residual nitrate from the wastewater. In September, the single stage nitrification-denitrification system was operated with methanol addition for complete nitrogen removal. The $FeCl_3$ addition for phosphorus removal, employed in primary treatment in August, was discontinued to increase the COD/TKN ratio entering the biological reactor and to ensure maximum nitrogen removal. Methanol was added on September 5 into the third, previously unused, anaerobic basin of the biological reactor and was continued until September 12, at an average dosage of 18.6 mg/l. The methanol was sufficient to supply the organic carbon needed for complete denitrification. The small aerobic basin following the anaerobic basin was also placed on stream.

With methanol addition, the residual TKN and ammonia in the effluent immediately increased. The TKN residual continued to increase throughout the month of September, even after the CH_3OH dosage was discontinued. Because of the observed loss of nitrification in the single stage nitrification-denitrification system, laboratory studies on methanol addition were performed on samples of nitrifying sludge from the nitrification process in the pilot plant's three stage activated sludge system. The methanol addition clearly inhibited the batch nitrification kinetics of the nitrifying sludge and confirmed the loss of nitrification observed in the single stage nitrification-denitrification system. It is not known whether acclimation of the nitrifiers to methanol could be developed. Since the glucose added as a control in the laboratory nitrification tests did not alter the laboratory nitrification kinetic rate, organics compatible with the nitrifying organisms can be substituted for methanol to complete the denitrification. These organics, such

Table VI. EFFECT OF ADDING $FeCl_3$[a] AND OF TERTIARY FILTRATION

Effluent	COD		S S		P		N	
	mg/l							
	July	Aug.	July	Aug.	July	Aug.	July	Aug.
Raw	250	319	153	197	5.86	5.42	18.7	19.1
Primary	119	112	73	58	3.10	2.67	15.1	14.9
Secondary	21	17	9	10	1.14	0.83	4.9	6.0
Filtered[b]	15	14	5.8	7.4	0.46	0.40	4.3	4.4

[a] 45 mg/l of $FeCl_3$ added ahead of primary clarifier.

[b] Dual media filters: 24 in. of 1.2- to 1.4-mm coal over 12 in. of 0.6- to 0.7-mm sand.

Table VII. SETTLING AND SOLIDS PRODUCTION

	Overflow Rate, m/d	Underflow Solids, mg/l	SVI, ml/gm	Solids Produced, gm/gm Applied BOD	
				Total	Wasted
Jan.	12.3	10,200	245	-[a]	-[a]
Feb.	12.6	10,100	250	.63	.49
March	12.3	6,720	330	.92	.71
April	12.3	6,760	277	-[a]	-[a]
May	14.1*	10,600	227	.80	.70
June	17.4	11,500	188	.77	.70
July	22.2	9,894	133	1.11	0.94[b]
August	23.1	8,927	134	-[a]	-[a]
Sept.	23.1	9,940	121	-[a]	-[a]

[a] Solids production not given because of solid accumulations or unknown solids losses. In September, optional reactor basins were placed on stream.

[b] The solids production reflects increased wasting to control F/M for decreased influent food.

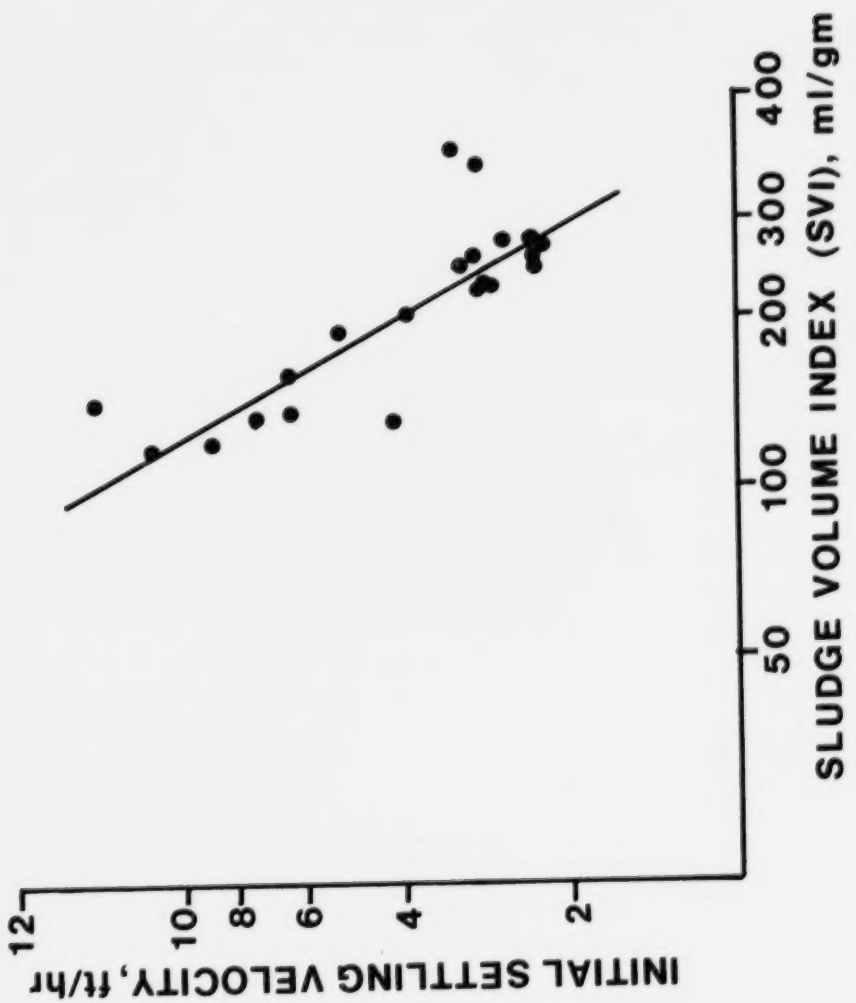


Figure 3. Initial settling velocity and the SVI

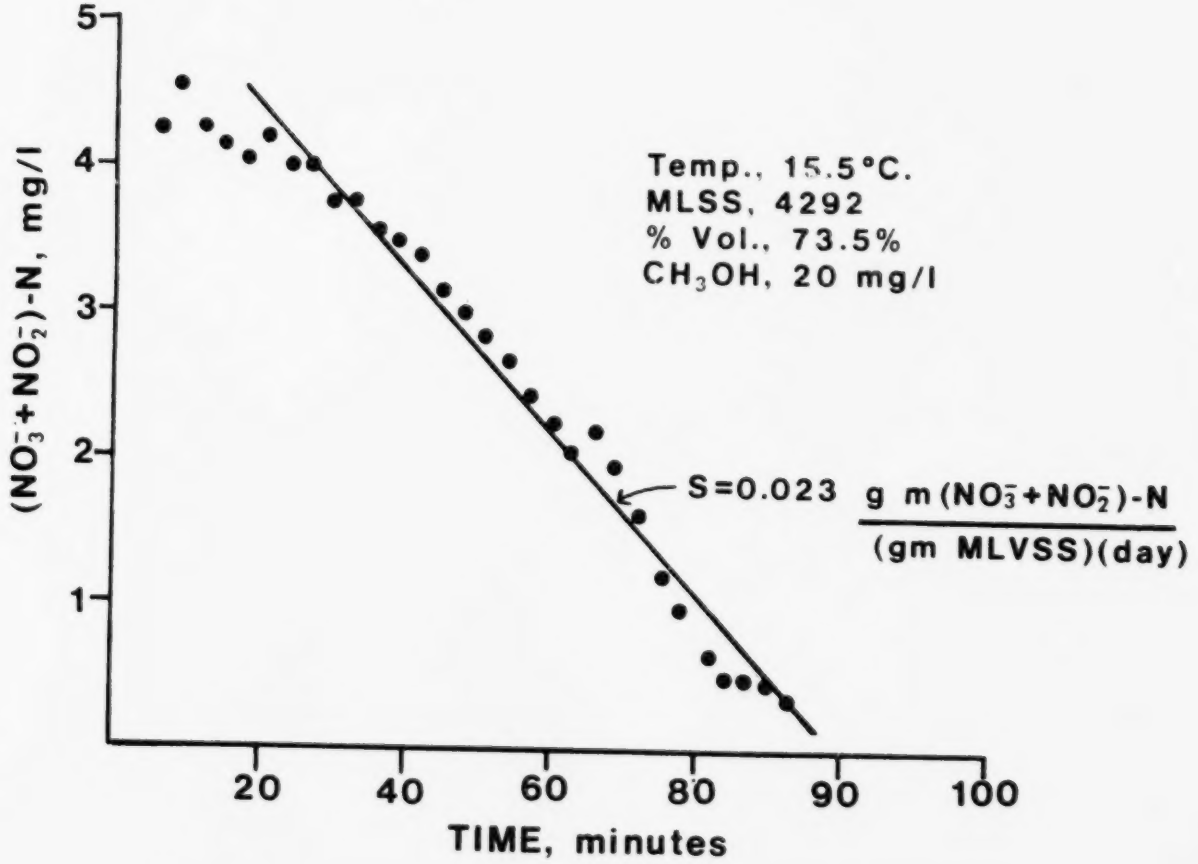


Figure 4. Methanol denitrification of residual $(NO_3^- + NO_3)$-N

as primary sludge, may be added either in the second basin of the process or into the optional small anaerobic basin to increase residual nitrogen removal.

SECTION VII

NITRIFICATION-DENITRIFICATION KINETICS

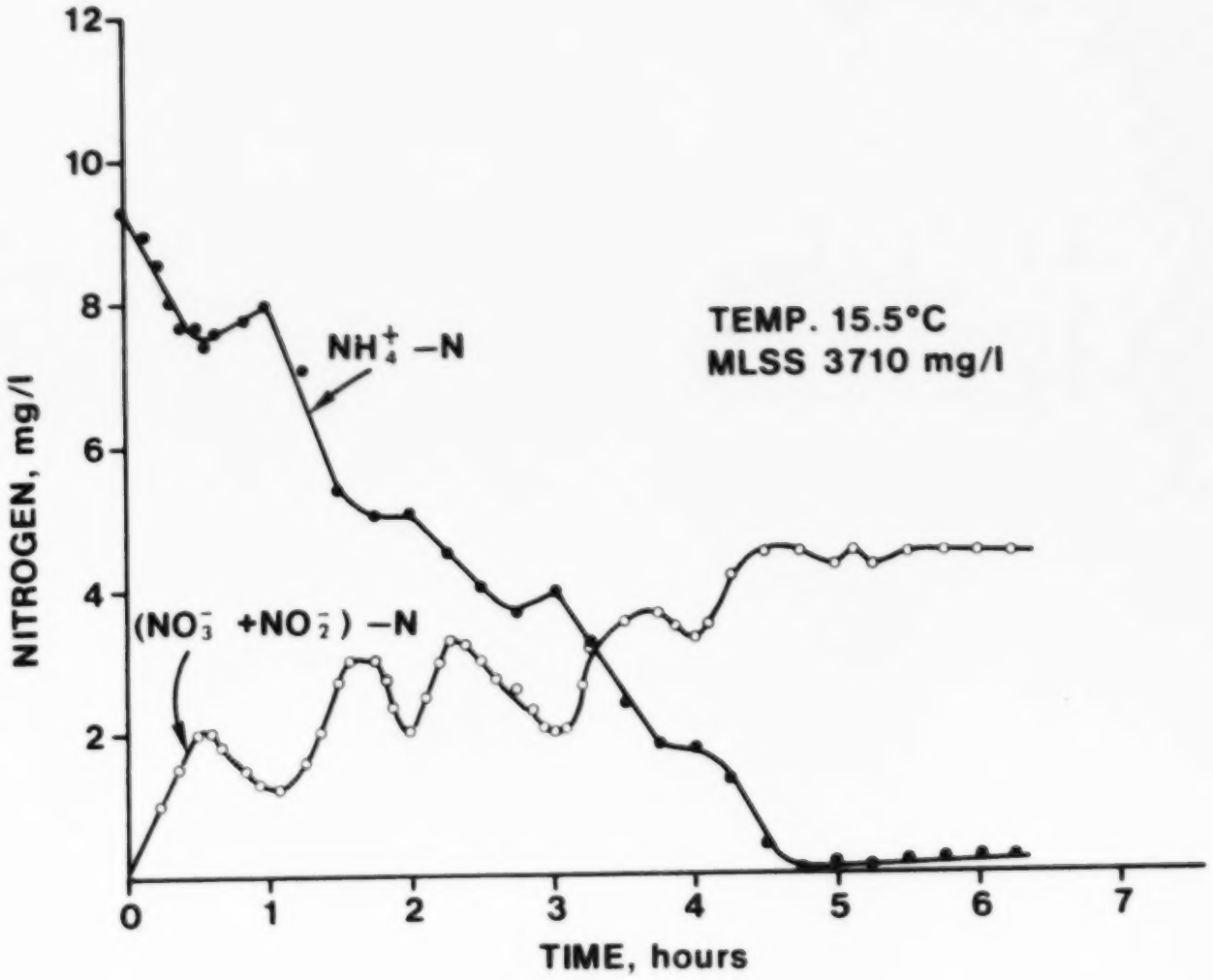
Batch laboratory nitrification-denitrification kinetic tests were performed periodically during the study. The typical cycling of the nitrogen species during the laboratory tests with on-off aeration is shown in Figure 5. The laboratory batch kinetic rate constants from these laboratory tests are summarized in Table 8. In the winter (15°F), the initial nitrification and denitrification rate constants were approximately similar in value and suggest equal time periods of aerobic and anaerobic conditions for most efficient operation. In contrast in summer, the nitrification rate constant was clearly higher than the denitrification rate constant. Thus, denitrification required more time than nitrification and controlled the reactor size.

Careful examination of the rate constants and the rate plots (Figure 5) also revealed that the nitrification rate constant tended to be similar through complete removal of the ammonia. The initial denitrification rate constant tended to decrease as the batch reaction continued. The maximum batch denitrification rate constant persisted for about one anaerobic period in the warm weather and, in winter with slower carbonaceous activity, extended into the second anaerobic period of the on-off cycle. Lower rates occurred for subsequent anaerobic periods and tapered off to immeasurable levels even though substantial (3 to 4 mg/l NO_3-N remained in the water, as shown in Figure 5.

An effect of the COD/TKN ratio also occurred in the batch kinetic studies. In June at 25°C with a COD/TKN ratio of approximately 10:1, the denitrification rate constants, although lower than the nitrification rate constant exhibited easily measurable values through four aerobic-anaerobic cycles. Through July and August with COD/TKN ratios of about 7.5:1, the initial cycle denitrification rate constant exhibited a decreasing value. The decreasing value of the denitrification rate constant probably was produced by a gradual shift in the organism population distribution of the mixed liquor and by the decreased availability of indigenous organic carbon. At the low F/M conditions. A shift in the population distribution should occur with both the decreasing COD/TKN or COD/NH_3-N ratio and with continued summer operation.

The subsequent values of the denitrification rate constants during repetitive aerobic-anaerobic cycling were also difficult to measure at the low COD/TKN ratio. With the cycle time in an August test (26.5°C) providing 30 min of aeration and 60 min of anaerobic activity, the endogenous denitrification rate constant was estimated at 0.0075 gm N/gm MLVSS/day.

Clearly, as the organics in the water during the batch test were depleted by the biological activity, the denitrification rate decreased. Thus the denitrification kinetic behavior in the batch laboratory reactor supported the observation that the decrease in nitrogen removal during July and August was significantly related to the decrease in the COD/TKN concentration ratio in the wastewater entering the biological reactor.



Fifure 5. Cyclic nitrification and denitrification

Table VIII. BATCH KINETICS FOR CYCLING[a] AEROBIC-ANAEROBIC CONDITIONS

	Temp., °C	gm N/gm MLVSS/Day				
		k_1	k_2	k_3	k_4	k_5
Nitrification						
2/22/73	15.5	0.032	0.042	0.016	0.026	0.035
6/28/73	25.0	0.083	0.095	-	-	-
7/20/73	27.0	0.11	0.11	-	-	-
8/24/73	26.5	0.12	-	-	-	-
Denitrification						
2/22/73	15.5	0.032	0.029	0.021	0.019	-
6/28/73	25.0	0.055	0.030	0.033	0.030	-
7/20/73	27.0	0.042	-	-	-	-
8/24/73[b]	26.5	0.026	0.0075[b]	-	-	-

[a] 30-min cycle of aerobic-anaerobic operation.

[b] Cycle altered; 30 min aerobic, 60 min anaerobic.

SECTION VIII

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